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(54) **Title:** METHOD IN THE MANUFACTURE OF STEEL

(57) **Abstract:** Method in the manufacture of steel, especially stainless steel, one or more metal-containing residues from the steel manufacturing process being mixed with an admixture which has a content of a substance in group 14 of the periodic system, following which the mixture is allowed to solidify and the mixture thus solidified is returned to a steel melt in connection with the manufacture of steel. The said residues preferably comprise a metal-containing hydroxide sludge from a steel pickling stage and/or metal-containing, finely dispersed or powdery residues from the steel manufacturing process.

METHOD IN THE MANUFACTURE OF STEEL

TECHNICAL FIELD

The present invention relates to a method in the manufacture of steel, especially stainless steel, by means of which method a metal content of residues from the steel manufacturing, such as hydroxide sludge from pickling and/or finely dispersed or powdery residues containing metals from the steel manufacturing process, are recovered.

DESCRIPTION OF THE PRIOR ART AND THE PROBLEM

Extremely large quantities of waste/residues are produced in connection with the manufacture of steel, here exemplified by the manufacture of stainless steel but also occurring in the case of carbon steel. Conventionally a large proportion of these waste products, such as various dusts containing metals and metal oxides, must be transported to special plants for reprocessing, in which, for example, resmelting is carried out in a number of stages. This is expensive, environmentally harmful (due to the transporting) and energy intensive. In principle it should be possible to return these dusts containing metals directly to the steel smelting process, but the problem is that their powdery form means that they create a pother, which presents major problems when mixing them into the steel melt. If this is attempted, they instead end up in the filters, which obviously does not have the desired effect.

Other residues, on the other hand, cannot be handled at all as things stand, but are simply deposited on waste tips, which represents a major environmental problem for the future. This is the case, for example, with acid, pickling fluid contaminated with metals emanating from the pickling process. Such used pickling fluid is at present handled by neutralising it with milk of lime, draining to a dried solids content of around 40-60% by weight (known as hydroxide sludge, neutralisation sludge or hydro-sludge) and depositing on waste tips. However, rain causes metals and acid residues to continuously leach out of the tip, so that constant attention must be paid to the leach water. It is particularly difficult to deal with used pickling fluids that contain acid mixtures, that is to say a mixture of nitric acid

(HNO_3) and hydrofluoric acid (HF), due to the fluoride content. The content of, for example, iron, chromium and nickel hydroxides used in stainless steel production also constitutes a handling problem. Nor would it be possible to recover the hydroxide sludge by mixing it into the steel melt as it is, since the high water content would lead to steam explosions.

FR 2 771 316 shows the treatment of metal hydroxide sludge from the manufacture of carbon steel. In the treatment, fine metallic material containing oil together with lime, among other things are added to the metal hydroxide sludge, following which the mixture is allowed to solidify for 2 to 30 days through exothermic reaction between the lime, water and oil. The solidified product is then crushed and preferably granulated, following which it can be returned to the steel manufacturing process in converters, for example. The use of lime, however, carries a number of disadvantages such as the corrosive, alkaline effect on linings.

DE 34 14 400 relates to a method in which hydroxide sludge is mixed with a hydraulic binder (in the example, cement), following which it goes for tipping.

JP 6184798 (abstract) relates to the sedimentation and centrifuging of iron hydroxide sludge with the object of being able to recycle the electrolyte.

WO 97/16573 describes agglomeration of fine iron oxide waste materials from e.g. pickling fluid that has been used in steel galvanisation. The iron oxide waste, which also contains iron hydroxides, is mixed with a source of calcium ions, e.g. chalk, a binder, water and optionally some form of carbon. The agglomerates formed can be us in metal manufacturing.

DE 41 01 584 describes the manufacture of briquettes from mill scale. The mill scale is mixed with a binder in the form of molasses and a catalyst in the form of calcium

hydroxide. The briquettes may be used instead of scrap or ore in steel manufacturing in a converter or directly in a blast furnace.

SUMMARY OF THE INVENTION

An object of the present invention is to present a method for handling metal-containing residues from the manufacture of steel, such as acid, metal-contaminated pickling fluid that is obtained as residue from the manufacture of steel, the metals in the residues being recycled to the steel production process. An object of the invention is furthermore to present a method of similarly handling hydroxide sludge which originated from acid, metal-contaminated pickling fluids and has already been dumped, and also of recovering its metals content. Yet another object of the invention is also to handle residues containing metals and/or metal oxides and/or metal hydroxides otherwise resulting from the steel manufacturing process, primarily finely dispersed or powdery residues, and to recycle the metals content thereof in the steel manufacturing process. The invention was primarily developed for use in connection with the manufacture of stainless steel, but can also be used in connection with other steel manufacturing, such as the manufacture of carbon steel.

These and other objects are achieved by means of the method according to the invention, as specified in claim 1.

The invention is based on the idea that metal-containing residues, comprising a metal-containing hydroxide sludge from a pickling stage for the steel, which hydroxide sludge comprises at least one fluoride-containing compound, can be returned to the steel production process, to a steel melt, when they have been mixed with an admixture having content of a substance from group 14 of the periodic system, particularly carbon and/or silicon. The admixture suitably has a content of the said substance in group 14 of the period system of at least 5 % by weight, preferably at least 10 % by weight, even more preferred at least 15 % by weight, even more preferred at least 30% by weight, even more preferred at least 35% by weight, and most preferably at least 40% by weight and up to 100% (excluding any water). The admixture is preferably made in the form of a,

beneficially viscous, liquid. Solid substances may also be used, however, preferably in powder form, such as pure carbon in the form of charcoal or some other form.

Liquids that have been tested with good results consist of water glass (Na_2O *x SiO_2, x = 3-5) and/or molasses. It is assumed that a reaction occurs with the water glass, in which reaction the water in the residue mixture is bound by the water glass, the residues being bound together and solidifying/hardening. The admixture according to the invention in this case therefore consists of a hardening admixture. The same thing happens if silicon dioxide (SiO_2) in solid form, e.g. powder form, is added, which represents an alternative embodiment of the invention. When mixing with molasses, which has a high carbon content, it is assumed that a polymerisation occurs in connection with the removal of water, which causes the mixture to solidify. It may also be assumed that the admixture acts as a reducing agent.

According to one embodiment of the invention, the object thereof is to use the admixture to convert the hydroxide sludge, which has been obtained by neutralising acid, metal-contaminated pickling fluids, into essentially solid form with a water content of no more than 15% by weight, preferably no more than 10% by weight, before returning it to the steel production process.

According to a preferred embodiment of the invention the admixture is mixed both with hydroxide sludge and with residues containing metals and/or metal oxides and/or metal hydroxides, which are finely dispersed or occur in powdery form, following which the mixture is allowed to set to solid form with a water content of no more than 15% by weight, preferably no more than 10% by weight, and then transferred to the steel production process.

The initial mixture of the hydroxide sludge and/or metal dusts and the admixture has a mud-like consistency, which solidifies within 24 hours. When using molasses, solidification normally occurs within 15 hours and when using water glass even faster. The

solidified product can then be mixed into the steel, preferably in connection with the steel smelting in an arc-furnace, the metals in the product going down into the steel melt, carbon being given off as carbon dioxide and water being given off as steam (in small amounts), and silicon, oxides, fluorides etc. in the product being taken up in the slag. The quantity of slag-forming material added to the steel melt can thereby advantageously be reduced, which also means that there is no overall increase in the quantity of slag formed.

DETAILED DESCRIPTION OF THE INVENTION

Used, acidic, metal-contaminated pickling fluids, which can be handled according to the invention, consist both of chemical pickling fluids and of pickling fluids for electrolytic pickling. These used pickling fluids consist of acid residues, such as hydrofluoric acid, nitric acid, sulphuric acid, phosphoric acid, salts of these acids, and dissolved out metals and metal oxides. In the method, the used pickling fluids are neutralised, in a known manner, to a pH value of approximately 9-10, through the addition of alkali, usually milk of lime, although other alkaline additives may also be used. The neutralised pickling fluid is then drained, suitably by mechanical means in a filter press, for example, to a dry solids content of at least 30% by weight, preferably at least 40% by weight and up to 80% by weight, normally to a maximum of 70% by weight. The drained product is called hydroxide sludge. The hydroxide sludge contains, for example, CaF_2, sulphates and Fe, Cr, Ni and Mo hydroxides, at least where hydrofluoric acid has been used in the pickling fluid and where the steel production relates to stainless steel.

Shot blasting oxide and grinding filings represent typical examples of residues containing metals and/or metal oxides and/or metal hydroxides resulting from the steel manufacturing process, which can be used for mixing into the hydroxide sludge. Shot blasting oxide and grinding filings contain metals, metal hydroxides and metal oxides, often of the spinel type, for example $Fe(FeCr_xO_y)$, where x=1-2 and y=2-4. Used shot blasting abrasives, for example, which is a form of blasting sand comprising iron shot, can also be mixed in. Cuttingslag from continuous casting plants or fabrication treatment can also be used. Other examples of substances that can be used are certain filter dusts, flue gas dusts and cooling

stage extracts, provided that these do not contain excessively high contents of unwanted substances, such as As, Zn or Pb. It is an advantage if the admixtures containing metals and/or metal oxides and/or metal hydroxides are finely dispersed, especially in powdery form or in the form of chips, for example.

The admixture according to the invention, which causes the hydroxide sludge and optional metal substances to harden, solidify or polymerise into an essentially solid product, accordingly consists of an admixture with a content of a substance in group 14 of the periodic system, in particular carbon and/or silicon.

The mixture of hydroxide sludge, residues in finely dispersed form or powdery form and the admixture according to the invention may comprise from 1% by weight up to 50% by weight, preferably up to 40% by weight and even more preferably up to 30% by weight of hydroxide sludge and/or from 1% by weight up to 90% by weight, preferably up to 80% by weight and even more preferably up to 70% by weight of residues in finely dispersed form or powdery form, and up to 55% by weight, preferably at least 10% by weight and even more preferably at least 15% by weight of admixture according to the invention. Optionally, aluminium may also be mixed in with a content of from 0.1 to 5% by weight. Altogether, the said ingredients preferably form 100% by weight of the mixture, it being naturally understood that neither the maximum content quoted nor the minimum content quoted can exist at the same time. Nor must the use of other ingredients be precluded, the ingredients stated here, however, constituting at least 80% by weight and more preferably at least 90% by weight of the mixture.

The mixture should be well stirred before being allowed to solidify. In the mixing, or prior to mixing, any lumps or "cakes" of the hydroxide sludge should be crushed and it should likewise be ensured that other residues used are present in finely dispersed form.

According to one embodiment of the invention the mixture, which immediately after mixing together has a loose mud-like consistency, is poured into vessels to solidify, the

vessels preferably being introduced into the steel melt together with the mixture, which has solidified normally no more than approximately 24 hours after mixing. Such vessels may themselves be composed of residues, suitably wood fibre, cellulose fibre or metal-based vessels, such as waste cardboard tubes or other cardboard products such as waste paper drums, or metal vessels. Examples of metal vessels that can be used include scrap that is to be melted down for manufacturing steel, waste steel or aluminium pipes etc. One variant alternative to filling vessels with the mixture is naturally to granulate it. Another alternative is to simply pour the mixture into a mould or directly onto a base, such as a concrete base. When the mixture solidifies it comes loose, which process can be facilitated, for example, by a coating or a layer of powder in the mould or on the base.

The solidified product is preferably mixed into the steel during the smelting of scrap in the arc furnace, but it is also feasible to mix in the solidified product in a converter. Admixtures of from 1% by weight up to 50% by weight of solidified mixture in the scrap metal are conceivable, even though smaller quantities are normally used, for example up to 40% by weight or preferably up to 30% by weight, calculated on the scrap or other steel raw material plus the solidified product according to the invention.

As an alternative to using aluminium admixtures in the mixture, as "primer" in order to start the steel smelting in the arc furnace, aluminium can be added together with the solidified mixture in the smelting process. If the mixture is placed in aluminium tubes to solidify, no extra aluminium admixture is generally required. Additional carbon (in the form, for example, of wood, coke, charcoal, paper, iron with a high carbon content or the like) can also be mixed in to act as reducing agent, especially where the admixture according to the invention is not composed of pure or essentially pure carbon, for example where the admixture according to the invention comprises water glass. Carbon from graphite electrodes, for example, can also be mixed in. It is, however, not always certain that additional carbon needs to be mixed in, especially not when molasses is used in the mixture.

The water content of the solidified product should be as low as possible. It is fine to mix the solidified product into the steel melt at water contents of up to 15% by weight, preferably 10-15% by weight and even better less than 10% by weight

EXAMPLES

In a series of tests, samples of hydroxide sludge and powdery or finely dispersed residues containing metals/metal oxides/metal hydroxides were mixed with molasses and carbon (Test series 1), water glass and carbon (Test series 2) and molasses and water glass (Test series 3). The mixtures were allowed to solidify and then melted down together with aluminium and iron, with the object of simulating large-scale smelting in an arc-furnace. Tables 1-3 show the composition of the various mixtures and the molten material in the form of percentage Cr, Fe and Ni and the yield of CR and Ni in the product obtained.

Test series 1

Table 1a

	kg	%	Cr(kg)	Ni(kg)
Shot blasting dust	1.00	16.00	0.20	0.08
Dust – cooling line	1.00	16.00	0.20	0.08
Grinding filings (hot grinding)	1.00	16.00	0.20	0.08
Hydroxide sludge	0.50	8.00	0.01	0.00
Shot blasting abrasives (used)	1.00	16.00	0.02	0.01
Coke	0.50	8.00		
Molasses	1.25	20.00		
Total weight (sample) =	6.25	100.00	0.630	0.250

16.8 g of solidified sample were weighed in together with 40.5 g Fe and 0.6 g Al, which were then melted down for a melting time of 4 minutes to a molten weight of 46.7 g. The degree of fusion was good. The resulting material and yield are shown in Table 1b. In

Table 1b the yield of Cr and Ni relates to the proportion of Cr and Ni that ended up in the molten steel.

Table 1b

	Weight	Yield
Cr	0.66%	20.67%
Fe	97.98%	
Ni	0.66%	52.10%
Remainder =	0.70%	
Total =	100.00%	

Test series 2

Table 2a

	kg	%	Cr(kg)	Ni(kg)
Shot blasting dust	1.00	16.67	0.20	0.08
Dust – cooling line	1.00	16.67	0.20	0.08
Grinding filings (hot grinding)	1.00	16.67	0.20	0.08
Hydroxide sludge	0.50	8.33	0.01	0.00
Shot blasting abrasives (used)	1.00	16.67	0.02	0.01
Coke	0.50	8.33		
Water glass	1.00	16.67		
Total weight (sample) =	6.00	100.00	0.630	0.250

13.3 g of solidified sample were weighed in together with 40.8 g Fe and 0.7 g Al, which were then melted down for a melting time of 4 minutes to a molten weight of 44.1 g. The degree of fusion was good. The resulting material and yield are shown in Table 2b. In

Table 2b the yield of Cr and Ni relates to the proportion of Cr and Ni that ended up in the molten steel.

Table 2b

	Weight	Yield
Cr	1,80%	58.44%
Fe	97.10%	
Ni	0.80%	65.45%
Remainder =	0.30%	
Total =	100.00%	

Test series 3

Table 3a

	kg	%	Cr(kg)	Ni(kg)
Shot blasting dust	1.00	18.18	0.20	0.08
Dust – cooling line	1.00	18.18	0.20	0.08
Grinding filings (hot grinding)	1.00	18.18	0.20	0.08
Hydroxide sludge	0.50	9.09	0.01	0.00
Shot blasting abrasives (used)	1.00	18.18	0.02	0.01
Water glass	0.50	9.09		
Molasses	0.50	9.09		
Total weight (sample) =	5.50	100.00	0.630	0.250

16.4 g of solidified sample were weighed in together with 28.3 g Fe and 0.8 g Al, which were then melted down for a melting time of 4 minutes to a molten weight of 31.1 g. The degree of fusion was good. The resulting material and yield are shown in Table 3b. In

Table 3b the yield of Cr and Ni relates to the proportion of Cr and Ni that ended up in the molten steel.

Table 3b

	Weight	Yield
Cr	1.69%	30.94%
Fe	96.68%	
Ni	1.25%	57.66%
Remainder =	0.38%	
Total =	100.00%	

Test series 4

Test series 4 aimed to analyse what becomes of the fluorides in the hydroxide sludge in implementing the invention

Table 4a

	kg	%	Cr(kg)	Ni(kg)	F(kg)
Shot blasting dust	0.50	5.56	0.10	0.04	0.00
Dust – cooling line	0.50	5.56	0.10	0.04	0.00
Grinding filings (hot grinding)	3.00	33.33	0.60	0.24	0.00
Hydroxide sludge	2.00	22.22	0.04	0.01	5.56
Shot blasting abrasives (used)	0.50	5.56	0.01	0.00	0.00
Water glass	2.00	22.22			
Molasses	0.50	5.56			
Total weight (sample) =	9.00	100.00	0.850	0.332	5.556

14.8 g of solidified sample were weighed in together with 43.4 g Fe and 0.9 g Al, which were then melted down for a melting time of 4 minutes to a molten weight of 48.2 g. The degree of fusion was good. The resulting material and yield are shown in Table 4b. In Table 4b the yield of Cr and Ni relates to the proportion of Cr and Ni that ended up in the molten steel. The yield of F on the other hand relates to the proportion of F that ended up in the slag, advantageously and desirably implying that, broadly speaking, all the fluoride present in the hydroxide sludge has ended up in the slag and not in the steel itself

Table 4b

	Weight	Yield
Cr	0.30%	10.96%
Ni	0.90%	84.15%
F	9.00%	99.51%

The greatest benefit with the method according to the invention is probably the facility for handling hydroxide sludge deriving from used pickling fluid, especially used pickling fluid that contains fluorides and which originates from the manufacturing process for stainless steel. According to the invention, the facility is also provided for handling hydroxide sludge that has already been tipped, it being possible in the long term to get rid of such existing tips. Another important advantage with the method according to the invention is naturally the ability to readily recover powdery or finely dispersed residues containing metals and/or metal oxides and/or metal hydroxides in the manufacture of steel. It is of particular advantage that Ni, Cr and Mo can be recovered from the residues. In addition the quantity of slag formers added to the steel melt is reduced, whilst no more slag than normal is formed as a result of the addition to the steel melt.

CLAIMS

1. Method in the manufacture of steel, especially stainless steel, one or more metal-containing residues from the steel manufacturing process being mixed with an admixture having a content of a substance in group 14 of the periodic system, following which the mixture is allowed to solidify and the mixture thus solidified is returned to a steel melt in connection with the manufacture of steel, **characterised in that** the said one or more residues comprise a hydroxide sludge containing metal from a pickling stage for the steel, which hydroxide sludge comprises at least one fluoride-containing compound.

2. Method according to claim 1, **characterised in that** the said admixture has a content of a substance in group 14 of the periodic system of at least 5 % by weight, preferably at least 10 % by weight, and even more preferably at least 15 % by weight and up to 100%.

3. Method according to claim 1 or 2, **characterised in that** the said admixture has a carbon and/or silicon content, the said admixture preferably consisting of a liquid, most preferably a viscous liquid, or an admixture in solid form, the said admixture preferably being selected from the group consisting of molasses, water glass, silicon dioxide and carbon.

4. Method according to any one of the preceding claims, **characterised in that** the said hydroxide sludge is made by neutralisation of used pickling fluid, following which the neutralised pickling fluid is drained to a dry solids content of at least 30% by weight, preferably at least 40% by weight and up to 80% by weight, preferably up to a maximum of 70% by weight of the said hydroxide sludge.

5. Method according to claim 4, **characterised in that** the said hydroxide sludge is retrieved from a waste tip.

6. Method according to any one of claims 4 to 6, **characterised in that** the said hydroxide sludge also comprises hydroxides of chromium and/or nickel and/or molybdenum; and/or metal sulphates.

7. Method according to any one of the preceding claims, **characterised in that** the said one or more residues comprise residues from the steel manufacturing process comprising metals and/or metal hydroxides and/or metal oxides, which residues preferably occur in finely dispersed form or powdery form and which residues are preferably selected from the group consisting of shot blasting oxide, grinding filings, shot blasting abrasives, cuttingslag, filter dusts, flue gas dusts and extracts from a cooling stage.

8. Method according to any one of the preceding claims, **characterised in that** aluminium is also added to the mixture.

9. Method according to any one of the preceding claims, **characterised in that** the mixture is made to comprise from 1% by weight up to 50% by weight, preferably up to 40% by weight and even more preferably up to 30% by weight of hydroxide sludge and/or from 1% by weight up to 90% by weight, preferably up to 80% by weight and even more preferably up to 70% by weight of metal-containing residues in finely dispersed or powdery form, and up to 55% by weight, preferably at least 10% by weight and even more preferably at least 15% by weight of the said admixture.

10. Method according to any one of the preceding claims, **characterised in that** the solidified mixture has a dry solids content of up to 15% by weight, preferably 10 to 15% and even more preferably less than 10% by weight.

11. Method according to any one of the preceding claims, **characterised in that** the mixture is poured into a vessel to solidify, the vessel preferably being introduced into

the steel melt together with the solidified mixture, and the vessel itself preferably being composed of a residue, preferably a wood fibre, cellulose fibre or metal-based vessel, even more preferably a vessel that is selected from the group consisting of cardboard products and metal scrap.

12. Method according to any one of the preceding claims, **characterised in that** the mixture is poured in a mould or onto a solid base to solidify, following which the solidified mixture is released from the mould or base.

13. Method according to any one of the preceding claims, **characterised in that** the mixture is returned to the said steel melt in quantities from 1% by weight up to 50% by weight, preferably up to 40% by weight and even more preferably up to 30% by weight, calculated on scrap or other steel raw material plus the solidified mixture.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 02/01473

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C22B 1/248
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9716573 A1 (WESTRALIAN SANDS LIMITED), 9 May 1997 (09.05.97), abstract --	1-13
A	DE 4101584 A1 (KOKEREIGESELLSCHAFT SAAR MBH), 23 July 1992 (23.07.92), abstract -- --------	1-13

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
28 November 2002	06-12-2002
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INTERNATIONAL SEARCH REPORT
Information on patent family members

28/10/02

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9716573 A1	09/05/97	AU 718757 B	20/04/00
		AU 7268396 A	22/05/97
		AU PN631595 D	00/00/00
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		AU PN933096 D	00/00/00
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